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A STUDY OF THE PIRIA REACTION

A THESIS

SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL

OF THE UNIVERSITY OF MINNESOTA

L. C.

BY

MURRAY MUNROE SPRUNG

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

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[Reprint from the Journal of the American Chemical Society, 53, 700 (1931).]

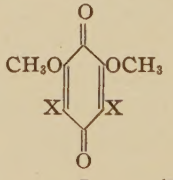
[Contribution from the School of Chemistry of the University of Minnesota]

A NEW TYPE OF OXIDATION PRODUCT DERIVED FROM QUINONES[1]

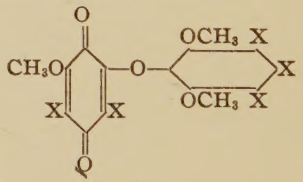
By W. H. Hunter and Murray M. Sprung

Received November 17, 1930 Published February 9, 1931

During a study of the oxidation of tribromo- and trichloropyrogallol-2, 6-dimethyl ether, Hunter and Levine[2] showed that when treated with any of a number of oxidants, these phenols gave both a yellow mononuclear quinone (I) and a red (or purple) phenoxy quinone (II).



I (X = Br or Cl)



II

However, when the oxidations were carried out with chromium trioxide in 50% acetic acid[3] there were obtained, in addition to these expected products, small amounts of colorless compounds. These compounds seemed to be of a nature different from any of the oxidation products previously isolated during this series of investigations. Their further study therefore

[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Murray M. Sprung in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September, 1928.

[2] Hunter and Levine, This Journal, **48**, 1608 (1926); cf. Hunter and Morse, *ibid.*, **48**, 1615 (1926).

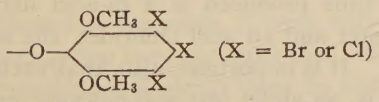
[3] Hunter and Levine, Ref. 2, p. 1612.

appeared to be of interest, and was undertaken, leading to the results described in the present paper.

A quantity of each of the colorless oxidation products was prepared and very carefully purified. On subjecting them to ultimate analyses and molecular weight determinations, a pair of empirical formulas was obtained which at first sight do not seem to be related. For the colorless oxidation product of tribromopyrogallol-2,6-dimethyl ether the best formula is $C_{28}H_{22}O_{15}Br_8$ (calculated molecular weight, 1238); for the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether the best formula is $C_{14}H_{11}O_8Cl_4$ (calculated molecular weight, 449). Nor do these formulas have any apparent relation to either of the normal products of oxidation of the phenols, for the mononuclear quinones have the composition, $C_8H_6O_4Br_2(Cl_2)$, while the dinuclear quinones have the composition, $C_{15}H_9O_6Br_5(Cl_5)$. Furthermore, the colorless substances are much richer in oxygen than any of the expected products. We were therefore led to suspect that oxidative rupture had occurred at some stage of these oxidations.

It was later discovered that the colorless compounds could also be obtained directly from the corresponding dinuclear quinones (II) of Hunter and Levine, by oxidizing the latter with chromium trioxide under conditions identical with those used in the synthesis of the colorless compounds from the trihalogenated pyrogallol-dimethyl ethers, showing that the colorless compounds are probably secondary products, derived from oxidation of the primary quinones.

A second very significant reaction was found to occur when dilute alkali was added to the colorless substances. Both compounds went into solution quite rapidly. On acidification of the solution, immediate precipitates of colorless materials were produced which were, *in both cases, different from the starting materials*. Investigation proved them to be the *original trihalogenated pyrogallol-dimethyl ethers* from which the colorless oxidation products, themselves, are derived. This action was very rapid, and in the case of the brominated compound it was demonstrated that the yield of phenol obtained was constant, that is, 63.2% of the weight of the brominated oxidation product used. It is therefore evident that the white compounds contain the residue



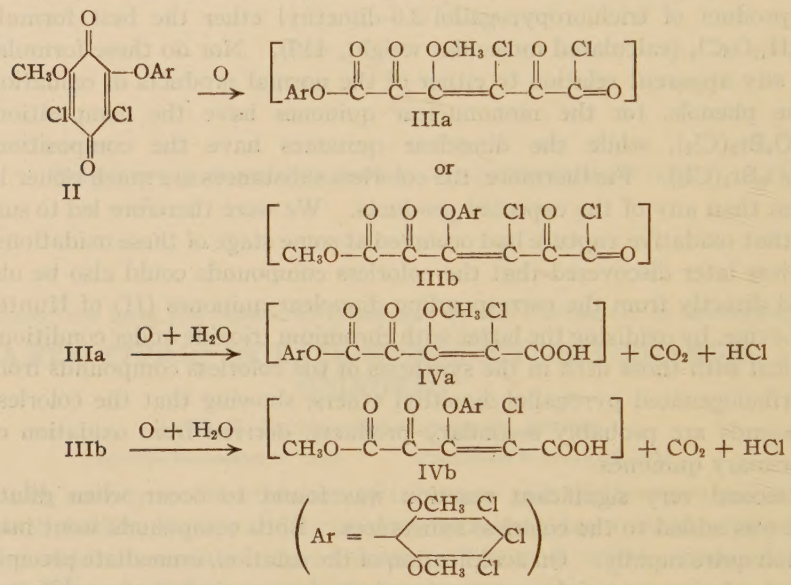
(X = Br or Cl)

and that this residue attaches to the rest of the molecule by some easily saponifiable linkage, for which only two simple possibilities suggest themselves: an ester linkage, and an acetal or hemiacetal linkage.

If now we consider the chlorinated oxidation product first (because of its simpler analytical formula, $C_{14}H_{11}O_8Cl_4$) we may arrive at a theory for its formation on the basis of the above information only. Three significant

facts must be accounted for at this time: first, one carbon atom is lost when the white compound is produced from the phenoxy quinone; second, the colorless compound still contains the phenoxy group as a distinct unit, easily lost by saponification; third, when the phenoxy residue is removed from the colorless compound, the resulting residue is easily and apparently completely destroyed by the reagent.[4]

A series of steps leading from the purple dinuclear quinone (II) to a product (IV) of the desired empirical composition is outlined below.



On the basis of the well-known oxidation of quinone to maleic acid,[5] it might reasonably be expected that if the chlorinated phenoxy quinone (II) were subjected to the action of a sufficiently strong oxidant, the first effect would be to split the quinonoid ring open at one of the double bonds. One oxygen atom would add to each side of the ruptured bond, and there would result one of two compounds, IIIa or IIIb, depending upon which double bond of the quinone ring was ruptured. Either of the hypothetical compounds thus produced is a di-acid derivative: the first a substituted phenyl ester and an acid chloride; the second a methyl ester and an acid chloride. It is important, also, that each is *twice an alpha oxo acid* derivative, that is, an alpha oxo acid chloride and an alpha oxo ester. Now alpha oxo esters are quite stable toward oxidation (pyruvic ester, for example). However, we have been able to find no mention in the literature

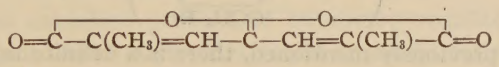
[4] Many attempts were made to isolate this residue after the "hydrolytic" reaction, but in no case could a single, homogeneous product be obtained. In all such cases, large amounts of halogen acid and some oxalic acid were found in the solution.

[5] Kempf, *Ber.*, **39**, 3719 (1906).

of the existence of alpha oxo acid chlorides. We consider it quite probable that such a compound, under the conditions of our experiments, would either be hydrolyzed to the free alpha oxo acid and then further oxidized, or oxidized directly as the oxo chloride. In either case, we should expect to find the carbon chain lessened by one carbon atom, to give a C_{14} compound. There would result, then, a complicated alpha oxo ester of an unsaturated 5 carbon di-acid (IVa or IVb).

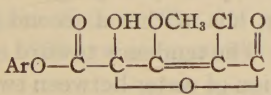
The formulas IVa and IVb are of course isomeric, and correspond empirically to the composition $C_{14}H_{10}O_8Cl_4$. The experimental formula for the chlorinated colorless oxidation product is $C_{14}H_{11}O_8Cl_4$, identical with the above except for one hydrogen, a discrepancy which could easily be accounted for by a relatively slight error in hydrogen analysis.

However, our colorless compound has no effect upon saturated sodium hydrogen sulfide, and it, therefore, cannot be a carboxylic acid. Furthermore, it forms a well-defined acetyl derivative, which can be crystallized unchanged from ethyl alcohol, and is, therefore, not a mixed anhydride. We conclude from this that our acid, which would be a gamma oxo acid, exists in the oxy-lactone form, similar to the alternate formula for levulinic acid, $CH_3C(OH)CH_2CH_2C{=}O$ (O). Levulinic acid, too, is known to form an acetyl derivative, which also can be crystallized unchanged from ethyl alcohol, and to which the formula $CH_3C(OCOCH_3)CH_2CH_2C{=}O$ (O) has been assigned.[6] Unsaturated gamma oxo acids show the same tendency toward lactone formation. Thus acetone dipyruvic acid exists only in the form of a dianhydro compound to which the formula

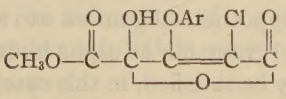


has been assigned.

If our white oxidation product is a gamma oxy lactone, it may have either of the following formulas



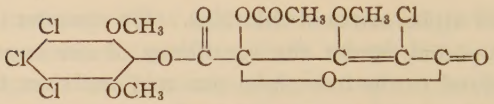
Va



Vb

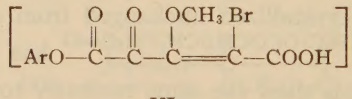
To choose between these two formulas, it need only be remembered that the substituted phenoxy group is easily saponified, the methoxy group not. Therefore the substituted phenyl group must be tied by an ester linkage, and the methyl group by an ether linkage. All this evidence points to formula Va as representing the most probable structure for the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether. Its acetyl derivative would then have the structure

[6] Bredt, *Ann.*, **236**, 225 (1886); *ibid.*, **256**, 314 (1890); Autenrieth, *Ber.*, **20**, 3191 (1887); Thiele, Tischbein and Lussow, *Ann.*, **319**, 184 (1901).

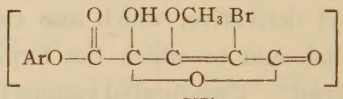


The colorless brominated oxidation product is similar to the chlorinated compound both as regards mode of formation and chemical behavior. The two compounds behave analogously in respect to a variety of chemical reagents. However, a series of carefully checked analytical data and molecular weight determinations has established the previously mentioned C_{28} formula, *i. e.*, $C_{28}H_{22}O_{15}Br_8$. Assuming the hydrogen analyses to be high again, we may modify this formula (for reasons which will shortly be clear) to $C_{28}H_{18}O_{15}Br_8$. If the brominated compound were exactly analogous to the chlorinated compound it would have the composition $C_{14}H_{10}O_8Br_4$. It is then evident that the formula $C_{28}H_{18}O_{15}Br_8$ represents a *dimolecular anhydride* of the simpler formula $C_{14}H_{10}O_8Br_4$.

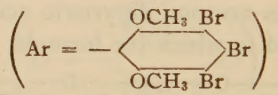
The most reasonable mechanism by which to explain the formation of the brominated oxidation product is as follows: as in the case of the analogous chlorine compound, a monomolecular derivative is first formed. This may possess either the free acid structure (VIa), or the gamma oxy-lactone form (VIb).



VIa



VIb



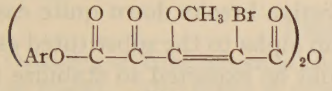
But, as we have previously mentioned, there is a definite tendency for the hydroxyl group of a gamma oxy lactone to become esterified through dilactone formation. When this is impossible, dehydration sometimes occurs, by loss of the hydroxyl group along with an alpha hydrogen atom. The above hypothetical gamma oxo acid, however, has neither a second gamma carboxyl group nor an alpha hydrogen atom. The tendency toward reaction can only be satisfied, in this case, by elimination of water between two molecules,[7] and this leads to the *dimolecular anhydride* which is actually isolated.[8]

There are at least three possible mechanisms by which the formation of a dimolecular anhydride may be explained, assuming that such anhydride formation actually does occur. There may be formed in the solution both

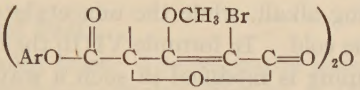
[7] Stating this in another way, the only "available" hydrogen atom which can split out with the hydroxyl group of one molecule is the hydroxyl hydrogen of a second molecule.

[8] The chloro and the bromo hypothetical intermediates, then, behave differently under the same experimental conditions. It is not entirely clear just why they should do so; but there is, on the other hand, no *a priori* reason to assume that they must behave the same.

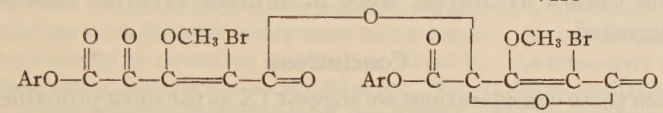
the free acid form and the lactone form (formulas VIa and VIb). The free acid, instead of becoming esterified intramolecularly, as in the case of the analogous chloro compound, may become esterified intermolecularly, and this may occur either by union with a second molecule of the free acid itself, or by union with a molecule in the oxy lactone form. In the first case, the ordinary type of acid anhydride (formula VIIa) would result; in the second case, the product would be an unsymmetrical molecule (formula VIIb).



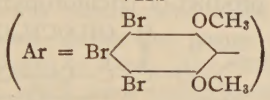
VIIa



VIIc

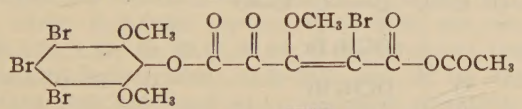


VIIb

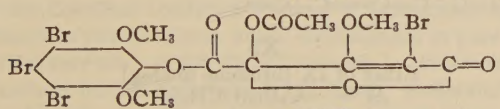


The third possibility is that only the lactone form of the acid (VIb) is involved in intermolecular anhydride formation. The dimolecular anhydride would then have the structure VIIc. It is possible to eliminate the first of these structures (formula VIIa) by virtue of the fact that the compound can be crystallized unchanged from ethyl alcohol, and therefore cannot be a normal acid anhydride. It is impossible at present to make a choice between formulas VIIb and VIIc.

The colorless oxidation product of tribromopyrogallol-dimethyl ether, like the analogous chloro compound, forms an acetyl derivative, when subjected to the action either of acetic anhydride and glacial acetic acid, or acetyl chloride and concentrated sulfuric acid.[9] This acetyl derivative has the composition $C_{16}H_{12}O_9Br_4$, and is therefore derived from the *monomeric form* of the acid. Its structure may be either that of a mixed anhydride VIIIa or an acetylated gamma oxy lactone VIIIb, again.



VIIIa



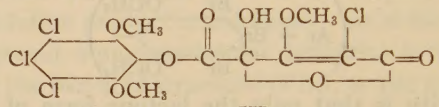
VIIIb

[9] The hydrogen necessary for this reaction may come from the sulfuric acid used during the acetylation. Very little water is required, due to the very large molecular weight of the colorless oxidation product.

We are once more inclined to favor the gamma oxy-lactone formula (VIIIb), by analogy with the acetyl derivative of levulinic acid and of our chlorinated oxidation product. Moreover, this acetyl derivative also may be crystallized unchanged from alcohol, which is evidence against the mixed anhydride formula. Further evidence for structure VIIIb is that whereas the acetyl derivative is broken down to the original phenol by dilute alkali, as is the white compound itself, in the former case the hydrolysis requires boiling alkali, while the unacetylated derivative breaks down quite easily in the cold. In formula VIIIb the oxo group alpha to the substituted ester grouping is modified in such a way as would be expected to stabilize the ester group toward hydrolysis, while in formula VIIIa no such modification is suggested.

Conclusions

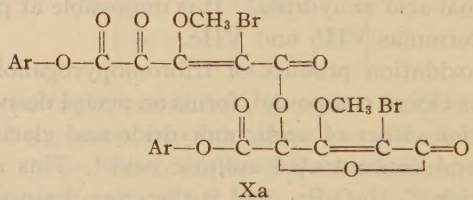
1. From these considerations we suggest IX as the most probable formula for the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether



IX

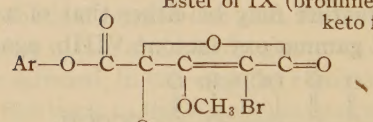
the oxy-lactone of α-chloro-β-methoxyquinonic[10] acid [(3,4,5-trichloro-2,6-dimethoxy)-phenyl ester].

2. Either Xa or Xb then becomes the best formula for the colorless oxidation product of tribromopyrogallol-2,6-dimethyl ether.

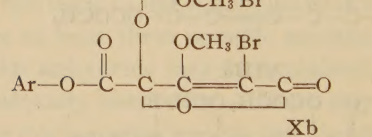


Xa

Ester of IX (bromine analog)



keto form



Xb

Ether of IX (bromine analog)

Ar = $-C_6Br_3(OCH_3)_2$

[10] In order to simplify the naming of these structures, it is convenient to designate the parent acid (α-keto-glutaconic acid, COOHCOCH=CHCOOH) by some suitable trivial name. We have adopted the name "quinonic acid," since a like oxidation of parabenzoquinone would yield this acid, if it could be carried out.

At the present time we wish to present these formulas provisionally only. Although these structures are as yet by no means rigorously established, we nevertheless consider them to be entirely plausible, in so far as they agree with *every one* of the known experimental facts and satisfy the analytical requirements admirably. We hope to be able to test these suggested structures by further chemical investigation of the substances and of analogous materials.

Experimental Part

Oxidation of Tribromopyrogallol-2,6-dimethyl Ether.—A representative procedure was as follows. Nine grams of tribromopyrogallol-2,6-dimethyl ether (m. p. 134.2°) was covered with 900 cc. of 50% acetic acid and warmed on a water-bath to 80°, at which temperature the dimethyl ether went into solution. Six and six-tenths grams (3 molar equivalents) of chromium trioxide was stirred in. An immediate precipitate of the purple phenoxy quinone was usually obtained. This varied somewhat in quantity, and in one or two cases no phenoxyquinone was formed. The temperature was maintained at 80° for fifteen to twenty minutes, after which the mixture was cooled, and filtered from the phenoxyquinone. It was then poured, slowly and with stirring, into 1200 cc. of cold water, and allowed to stand. The white oxidation product appeared as a very flocculent precipitate, which slowly settled to the bottom of the vessel. After several hours, most of the supernatant liquid was decanted, and the white compound filtered onto a good grade of coarse filter paper made into a "fluted filter." It was washed with dilute acetic acid, water and dilute (*ca.* 25%) alcohol and allowed to dry between filter papers. Eight oxidations, each starting with 9 g. of the phenol, gave an average of 2.9 g. of the colorless compound, or about 32% of the weight of the starting material. The yield was greatly reduced when the oxidation was carried out with larger amounts of the phenol.

The colorless compound melted, when crude, at 193–197°. A sample was purified by recrystallization, as follows: four times from dilute ethyl alcohol, once from aqueous ethyl acetate, three times from dilute methyl alcohol, twice from aqueous methyl acetate and finally once again from dilute methyl alcohol. Starting now with a bath temperature of 200°, the substance showed a melting point of 206–206.6° (with decomposition). A sample obtained from the last methyl alcohol–water filtrate by evaporating to dryness melted with decomposition at 206–207° (Jackson's test for purity).

Anal. Subs., 0.1842, 0.1977: AgBr (Carius), 0.2258, 0.2413. Subs., 0.1955, 0.2022: CO_2, 0.1940, 0.2006: H_2O, 0.0318, 0.0325. Subs., 0.1747, 0.1709: AgI (Zeisel), 0.1936, 0.1922. Calcd. for $C_{28}H_{18}O_{15}Br_8$(6 OCH_3): C, 27.23; H, 1.46; Br, 51.86; O, 19.45; OCH_3, 15.08; $C_8H_6O_3Br_3$ (hydrolyzable), 63.2; mol. wt., 1234. Found: C, 27.06, 27.04; H, 1.81, 1.80; Br, 52.17, 52.04; O (by difference), 19.96, 20.12; OCH_3, 14.64, 14.86; $C_8H_6O_3Br_3$ (hydrolyzable), 63.2, 63.3; mol. wt. (in ethylene dibromide), 1241, 1208, 1215, 1110, 1150, 1260; mol. wt. (in camphor), 1226, 1515.

Properties of the Colorless Oxidation Product of Tribromopyrogallol-2,6-dimethyl Ether.—This substance crystallizes from dilute ethyl alcohol in pure white, microscopic needles, melting, when very pure, at 206–206.6° (decomp.). It is very soluble in acetone, acetic acid, ethyl acetate, methyl acetate and chloroform; moderately soluble in methyl alcohol, and ethyl alcohol; slightly soluble in amyl alcohol, toluene, benzene, xylene, ethylene dibromide, acetophenone and hot carbon tetrachloride; practically insoluble in cold carbon tetrachloride, water and ligroin.

It is oxidized only very slowly by hot alkaline permanganate, hot acid permanganate and boiling concentrated nitric acid. Boiling silver nitrate in 95% alcohol pro-

duces only a slight murkiness. It dissolves in concentrated sulfuric acid to a clear solution. Such a solution was diluted with water, leading to the precipitation of a white material, which was shown to be tribromopyrogallol-2,6-dimethyl ether (m. p. 131–136°).

The original oxidation product is entirely unaffected by any of the following reagents: boillng bromine in chloroform, phosphorus pentabromide in hot chloroform or carbon disulfide, liquid bromine without a solvent, dilute or concentrated hydrochloric acid, dilute nitric acid, saturated sodium hydrogen sulfide.

The Acetyl Derivative.—One and two-tenths grams of the white oxidation product was covered with acetyl chloride, 2 drops of concd. sulfuric acid added and the mixture heated gently in an acetylation flask for three hours. Fumes of hydrogen chloride were evolved from the start. The contents of the flask, poured into 200 cc. of ice water, gave 1.1 g. of the white acetyl derivative. Three recrystallizations from dilute ethyl alcohol gave a pure white product, m. p. 141–144° (decomp.). A sample recrystallized twice more was used for analysis.

Anal. Subs., 0.1261, 0.1889: AgBr, 0.1437, 0.2146. Subs., 0.1861, 0.1655: CO_2, 0.1964, 0.1743; H_2O, 0.0345, 0.0315. Calcd. for $C_{16}H_{12}O_9Br_4$: C, 28.45; H, 1.81; Br, 47.91. Found: C, 28.78, 28.72; H, 2.07, 2.13; Br, 48.16, 48.34.

The same acetyl derivative is obtained by using acetic anhydride and glacial acetic acid as the acetylating agent. It crystallizes from dilute alcohol in minute, colorless needles. It is moderately soluble in ethyl alcohol, methyl alcohol, glacial acetic acid, chloroform and carbon disulfide; slightly soluble in fractol or ligroin.

Action of Dilute Alkali upon the Acetyl Derivative.—A sample of the acetyl derivative, when boiled with 6% potassium hydroxide, slowly went into solution. When the solution was cooled and acidified with a few drops of concentrated hydrochloric acid, a white material precipitated, which was shown, by the method of mixed melting points, to be tribromopyrogallol-2,6-dimethyl ether.

The Action of Dilute Alkali upon the Colorless Oxidation Product.—An example is given of one of the hydrolytic experiments in which quantitative technique was adopted. Ninety-eight hundredths gram of the pure colorless oxidation compound was dissolved in 90 cc. of cold 6% potassium hydroxide. Solution required only a minute or two. Immediate acidification at this point would give a good yield of the tribromodimethoxyphenol; however, for the sake of quantitative results, the solution was heated gently on the steam-bath for two hours, then nearly neutralized with glacial acetic acid and made slightly acid with dilute (1 normal) acetic acid. The precipitate which resulted was allowed to stand overnight, then filtered onto a weighed Gooch crucible and dried over calcium chloride in a vacuum desiccator. The tribromopyrogallol-2,6-dimethyl ether weighed 0.62 g., or 63.3% of the weight of the starting material. A check determination gave 63.2%.

A sample of the phenol thus prepared was crystallized twice from dilute ethyl alcohol, giving pure white, delicate needles, m. p. 133.8–134.0°; mixed melting point with a known sample of tribromopyrogallol-2,6-dimethyl ether, 134–134.2°. Since it was exceedingly important to establish, without question, the identity of this material, the purified material was subjected to analysis.

Anal. Subs., 0.2002, 0.2037: AgBr (Carius), 0.2881, 0.2943. Subs., 0.0695, 0.0925: CO_2, 0.0664, 0.0841: H_2O, 0.0151, 0.0177. Calcd. for $C_6H_7O_3Br_3$: Br, 61.34; C, 24.87; H, 1.80. Found: Br, 61.24, 61.48; C, 25.00, 24.80; H, 2.35, 2.15.

Investigation of the Filtrate from the Hydrolysis Reaction.—Examination of the solution from which the tribromopyrogallol-dimethyl ether was filtered led to the following results. Silver nitrate and concd. nitric acid gave a heavy precipitate of silver bromide, showing that further decomposition occurred when the phenol was split off.

Chlorine water and chloroform also disclosed the presence of much free bromide ion. From the filtrate from one sample of 0.57 g. of the white oxidation product, 0.25 g. of silver bromide, equivalent to 0.10 g. of bromine or 33% of the total bromine present in the starting material, was obtained. This, plus the bromine content of the dimethyl ether, accounts for approximately the total bromine available. Another portion of the solution, when neutralized with ammonia and treated with a solution of calcium chloride, gave a white precipitate which gradually darkened on standing, indicating the presence of some reducing acid residue. This was confirmed by the fact that permanganate acidified with dilute sulfuric acid was rapidly decolorized.

The filtrate from one hydrolytic experiment was extracted with ether and the ether extracts allowed to evaporate. There was obtained less than 0.1 g. of an impure white material, melting at 150–160°. The substance was exceedingly deliquescent; standing in the air for even a few moments rendered it of a sirupy consistency. It could not again be isolated, even in this state of impurity, although several attempts were made to do so.

Hydrolytic Decomposition by Means of Other Alkalies.—The hydrolysis could be effected by the use of weaker bases than potassium hydroxide, for example, ammonia or aniline. The latter reagent had previously been used in attempts to obtain an anilide of the colorless compound, without success. It was now clear why these experiments had proved fruitless. If heated for a few minutes with aniline in alcoholic solution, the substance was unaffected. If heated for a somewhat longer time, a gummy product resulted, from which a quantity of the tribromodimethoxyphenol could be obtained. The effect of aniline when used without a solvent was either to leave the colorless material unaffected, or to cause deep-seated decomposition of the substance.

Oxidation of 3,5-Dibromo-6-methoxy-2-(3,4,5-tribromo-2,6-dimethoxyphenoxyl)-*p*-benzoquinone.—A sample of the above compound, obtained as a by-product during the oxidation of tribromopyrogallol-2,6-dimethyl ether to the colorless oxidation product, was recrystallized three times from glacial acetic acid. It melted at 219–219.5° (Hunter and Levine report 214°). When recrystallized again it melted at 219.5° sharply. Thirty-five hundredths gram of this material was suspended in 50 cc. of 50% acetic acid, heated to 80° and 0.2 g. of chromium trioxide added. The heating was continued for one and one-half hours, after which the solution was cooled and the unchanged quinone filtered. The filtrate was diluted with 120 cc. of water. A white substance slowly precipitated. After being filtered, washed and dried at 100°, it showed a melting point of 200.5–201.5° (only the most highly purified samples of the white product melt above this temperature) with decomposition, and was found to be identical with the white oxidation product obtained in the original oxidation experiments.

Oxidation of Trichloropyrogallol-2,6-dimethyl Ether.—A representative procedure was as follows. Three grams of trichloropyrogallol-2,6-dimethyl ether was dissolved in 350 cc. of 50% acetic acid and heated on a water-bath to 78°. Two grams (1.7 molar equivalents) of chromium trioxide was stirred in and the heating continued for ten to fifteen minutes, after which the mixture was cooled and the red phenoxyquinone filtered off. (As in the case of the corresponding bromo compound, this phenoxyquinone usually precipitated immediately upon addition of the oxidant, but it varied in amount, and in one or two cases it failed to appear at all.) The filtrate was poured into 500 cc. of cold water and allowed to stand overnight, when the white oxidation product had settled to the bottom of the beaker. Most of the supernatant liquid was decanted, and the precipitate was filtered onto a fluted filter paper, washed with dilute acetic acid, water and dilute alcohol and dried between sheets of filter paper. The average yield of crude material was 31% of the weight of the starting material. The crude material melted at 177–182° (decomp.). After crystallizing twice from dilute acetic acid, twice from

dilute ethyl alcohol and twice from dilute methyl alcohol, it melted at 187.4–187.8°, with decomposition.

Anal. Subs., 0.1059, 0.1003, 0.1391, 0.1270: AgCl (Carius), 0.1380, 0.1284, 0.1779, 0.1627. Subs., 0.1657, 0.1669: CO_2, 0.2300, 0.2297; H_2O, 0.0357, 0.0365. Subs., 0.2040, 0.2027: AgI (Zeisel), 0.3220, 0.3175. Calcd. for $C_{14}H_{10}O_8Cl_4$ (3 OCH_3): Cl, 31.65; C, 37.53; H, 2.25; O, 28.57; OCH_3, 20.76; mol. wt., 448. Found: Cl, 32.24, 31.67, 31.64, 31.69; C, 37.85, 37.53; H, 2.41, 2.45; O (by difference), 28.10, 28.33; OCH_3, 20.84, 20.68; mol. wt. (in ethylene dibromide), 525, 476, 460; mol. wt. (in camphor), 515.

Properties of the Colorless Oxidation Product of Trichloropyrogallol-2,6-dimethyl Ether.—This substance crystallizes from dilute alcohol in small, white, delicate needles, which melt, when very pure, at 187.4–187.8°, with decomposition. The microscopic crystals are much better developed than those of the bromine analog, which gives reason to suspect, *a priori*, a much smaller molecule in the former case than in the latter. It is readily soluble in ethyl alcohol, methyl alcohol, glacial acetic acid, acetone, chloroform and ether; slightly soluble in carbon disulfide, benzene, toluene, xylene and ethylene dibromide; practically insoluble in water, carbon tetrachloride and fractol.[11]

Like the bromine analog, the substance is inert to most common chemical reagents. It is unaffected by dilute or concentrated hydrochloric acid, dilute or concentrated nitric acid, saturated sodium hydrogen sulfide, bromine, pure or in solution, and is attacked only very slowly by hot acid or alkaline permanganate. The pure material dissolves in concentrated sulfuric acid to a clear solution. One such solution, on dilution, was found to give a precipitate of trichloropyrogallol-2,6-dimethyl ether (m. p. 121–122°). The same substance was produced by the action of 6% potassium hydroxide on the colorless product, and subsequent acidification, by dilute acetic acid, of the solution produced. It was identified by the method of mixed melting points. A large amount of free chloride ion was found to be produced during the hydrolytic reaction, and there was also present in the solution, after reaction, a substance which reduced acid permanganate. It could not be isolated.

Acetylation.—Fifteen-hundredths gram of the colorless compound and 30 cc. of acetic anhydride, contained in a long-necked flask, was warmed gently over a free flame for two to three hours. The contents of the flask were cooled, neutralized with sodium hydroxide and diluted with water. The brown product was crystallized from dilute alcohol, giving white crystals, m. p. 135–136°, with decomposition. A chlorine analysis on the crude product indicated that it was a monoacetyl derivative.

Anal. Calcd. for $C_{16}H_{12}O_9Cl_4$: Cl, 29.0. Found: 27.7, 29.0.

Oxidation of 3,5-Dichloro-6-methoxy-2-(3,4,5-trichloro-2,6-dimethoxyphenoxyl)-*p*-benzoquinone.—Five-tenths gram of the above compound was suspended in 100 cc. of 50% acetic acid, and treated at 78° with 0.35 g. of chromium trioxide. After heating at this temperature for one and one-half hours, the solution was cooled, the excess quinone filtered and the filtrate poured into 200 cc. of cold water. After twenty-four hours, the small amount of white material which had settled to the bottom of the vessel was collected, washed with water and dried. It melted at 186–188°, with decomposition, and was identical with the colorless oxidation product of trichloropyrogallol-2,6-dimethyl ether.

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[11] The oxidation product sometimes appears in the colloidal condition, either when first precipitated from 50% acetic acid by dilution, or on subsequent recrystallization. Under these circumstances, purification cannot be effected and the material must be discarded.

Summary

The oxidation of halogenated pyrogallol-2,6-dimethyl ethers leads to the formation of colorless products. The same products are likewise obtained by the further oxidation of phenoxy quinones, derived from the halogenated phenols by oxidation. These colorless compounds differ from previously known quinone oxidation products by virtue of the fact that in their formation by rupture of the quinone ring, only one carbon atom of the ring is lost.

Structures are proposed for these compounds, and the mechanism by which they are formed is discussed.

MINNEAPOLIS, MINNESOTA

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[Contribution from the School of Chemistry of the University of Minnesota]

THE PIRIA REACTION. I. THE OVER-ALL REACTION[1]

By W. H. Hunter and Murray M. Sprung

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Aminosulfonic acids can be obtained directly from aromatic nitro compounds by heating the latter with metal sulfites and then boiling with mineral acids. This reaction was discovered by Piria[2] in 1851, and will therefore be referred to in the following pages as "the Piria reaction." Piria, at that time, subjected α-nitronaphthalene to the action of ammonium sulfite in dilute alcoholic solution, and isolated two reduction products: the ammonium salts of naphthionic acid and of α-naphthylsulfaminic acid, respectively.

[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Murray M. Sprung in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September, 1928. Presented before the Division of Organic Chemistry of the American Chemical Society at the Minneapolis Meeting, September 9–16, 1929.

[2] Piria, *Ann.*, **78**, 31 (1851).

It would naturally be expected that this reaction would be of importance in the manufacture of intermediates for azo dyes and some such hope undoubtedly has inspired many workers, for in the eighty years which have intervened since its discovery, the Piria reaction has been studied by a large number of investigators.[3]

However, the information which has been obtained has been of a decidedly general nature. No systematic investigation, from a theoretical point of view, of a series of nitro compounds has been carried out; no two investigators have used identical procedures for carrying out the reduction, or for isolating the products. The original ammonium sulfite has in many cases been replaced by sodium or potassium sulfite of various concentrations, or by equally varied concentrations of bisulfite. Also, much of the information is in the usual none too clear specifications of an organic chemical patent of the early days.

Further, with the exception of Raschig,[4] no one has given any particular consideration to the mechanism of the changes involved.

Now the Piria reaction is carried out in two distinct stages: a reduction stage, in which the nitro group is known to be transformed into an amino group, a sulfaminic acid group, or both; and an acid treatment stage, in which an amine or an aminosulfonic acid appears. It is entirely fair, it would seem, to say that neither of these stages is understood, though many opinions have been expressed about both of them taken singly and together.

This situation is due primarily to the fact that most previous investigators other than Raschig, and perhaps Weil,[5] have been primarily interested in finding the best reagent and the best conditions for the production of a single desired compound, usually an aminosulfonic acid.

Aside from its value, or lack of it, as a source of intermediates, the

[3] The most important published articles and a number of the more significant patent citations are as follows: Hilkenkamp, *Ann.*, **95**, 86 (1855); Carius, *Z. Chem. Pharm.*, 632 (1861); Smit, *Ber.*, **8**, 1442 (1875); Nietzki, *ibid.*, **29**, 2448 (1896); German Patent 86,097, *Friedländer*, **4**, 90 (1895); Walter, German Patent 109,487, *ibid.*, **5**, 70 (1899); Turner, German Patent 123,115, *ibid.*, **6**, 171 (1900); Weil, German Patents 147,552 and 151,134, *ibid.*, **7**, 58 and 61 (1902); Weil and Moser, *Ber.*, **55**, 732 (1922); Weil and Wassermann, *ibid.*, **55**, 2533 (1922); E. and H. Erdmann, German Patent 65,240, *Friedländer*, **3**, 41 (1891); Willgerodt, *J. prakt. Chem.*, **32**, 117 (1885); Meister, Lucius and Brüning, German Patents, 92,082 and 215,338, *Friedländer*, **4**, 528 (1895), and **10**, 182 (1910); Alfred Fischesser and Company, German Patent 79,577, *ibid.*, **4**, 565 (1894); Bayer and Company, German Patent 113,944, *ibid.*, **6**, 184 (1900); Bucherer and Borsch, *J. prakt. Chem.*, [2] **111**, 329 (1925); Meister, Lucius and Brüning, German Patents 78,772 and 126,804, *Friedländer*, **4**, 305 (1894) and **6**, 384 (1901); Bayer and Company, German Patent 103,395, *ibid.*, **5**, 252 (1897); Raschig, "Stickstoff and Schwefel Studien," Verlag Chemie G. m. b. H., Leipzig, **1924.**

[4] Raschig, "Stickstoff and Schwefel Studien," Verlag Chemie G. m. b. H., Leipzig, **1924**, pp. 254–272.

[5] Weil and Wassermann, *Ber.*, **55**, 2533 (1922), and earlier references cited therein.

reaction presents interesting problems, as a study in oxidation–reduction, and as a problem in the effect of hydrogen-ion concentration.

However, the methods of carrying out the reaction have been so various that it was impossible to gain a viewpoint on previous work. It therefore seemed wise to set up certain standard conditions, into which any nitro compound would be forcibly fitted, both for the reduction stage and the acid-treatment stage, in order to arrive at some uniformity of treatment. This was done, and a series of eight somewhat coherently related nitro compounds was studied, under these standard conditions, as well as with some deliberate variation, in certain cases. In the discussion of this treatment it is convenient to use the terms "standard reduction," "standard acid treatment," and in addition, the term "over-all reaction," the latter referring to the use of both operations in sequence.[6]

The results of this preliminary survey of the reaction are set forth in the table. It will be noted that the standard procedure is not indicated for two of the nitro compounds. In these cases the standard procedure was used, but it failed to give satisfactory reduction, and the actual procedures are included, to illustrate the possibilities of variation, and as examples of the types of variation to be found in existing literature.

Discussion of the Results

It will be noted that in every case the over-all reaction produced an aminosulfonic acid, and in every case but one (*p*-nitrophenol)[7] an amine

[6] Standard Reduction.—To a weighed quantity of the nitro compound was added enough of a 5.2 *N* (2.6 *M*) solution of sodium bisulfite to constitute approximately 75% excess over that calculated on the basis of 3 moles of bisulfite per mole of nitro compound. Enough 5 normal sodium hydroxide was then added to neutralize one-fourth of the bisulfite, and to the whole was added water in the ratio of 1250 cc. for each mole of nitro compound. This mixture, contained in a round-bottomed flask, was heated to boiling under a reflux condenser (with continual mechanical stirring) until homogeneous. (At this time the odor of nitro compound should be no longer noticeable.)

Standard Acid Treatment.—The mixture was evaporated on the steam-bath to about half the original volume, and treated while hot with 250 cc. of concentrated (12 *N*) hydrochloric acid for each mole of original nitro compound. It was boiled for one-half to two hours, and then allowed to cool.

Isolation.—In all cases where the amine produced was volatile with steam, excess alkali was added at this point, and the amine distilled out in a current of steam. The sodium salt of the aminosulfonic acid usually crystallized from the cooled residue, since such sodium salts are quite insoluble in an alkaline salt solution of the concentration here produced. This method of isolating the products was varied whenever it was necessary or more convenient to use other means. The procedure was especially different in case of those reactions which gave rise to amines which are not volatile with steam. These reactions are described separately, as a general statement cannot be made about them.

[7] For reasons stated in the experimental part of the paper, we believe that very little, if any, amine was produced in this case.

TABLE I

NATURE AND QUANTITY OF PRODUCTS OBTAINED IN THE "OVER-ALL" PIRIA REACTION

Nitro compound	Experimental condition	Time for reduction phase, hours	Amine isolated	Av., %	Aminosulfonic acid isolated	Av., %	Other product isolated	Av., %
Nitrobenzene	St. proc.	1.25	Aniline	26	Sulfanilic	27	.....	..
α-Nitronaphthalene	St. proc.	5	α-Naphthyl-	2	Naphthionic	25	1-Naphthylamine-2,4-disulfonic acid	66
o-Nitrotoluene	Same	12	*o*-Toluidine	40	2-Toluidine-5-sulfonic	34	Sodium *o*-tolylsulfaminate	12
p-Nitrotoluene	Same	5	*p*-Toluidine	72	4-Toluidine-3-sulfonic	11	.....	..
Nitro-*p*-xylene	3 Times[a] usual amt. water	17	*p*-Xylidine	60	3-Amino-1,4-xylene-6-sulfonic	16	.....	..
m-Dinitrobenzene	*A* 10% excess Na_2SO_3(HCl used[c])	2	*m*-Nitroaniline	Tr.	*A m*-Nitraniline *p*-sulfonic	64	.....	..
	B 110% excess $NaHSO_3$(H_2SO_4 used)	8.5[b]	.....	..	*B m*-Nitraniline *p*-sulfonic	1	*m*-Phenylenediamine-*p*-sulfonic acid	10
p-Nitrobenzoic acid	St. proc.	4.5	*p*-Aminobenzoic acid	21[d]	*p*-Amino-*m*-sulfobenzoic	61[e]	.....	..
p-Nitrophenol	St. proc.	11[f]	.....	..	*p*-Aminophenol-*m*-sulfonic	14	.....	..

[a] When the normal amount of water was used, the reaction was found to be incomplete even after twenty or twenty-five hours of boiling. [b] The reaction was not complete at this time. [c] The standard reduction gave an abnormal reaction. [d] Isolated partly as such, and partly as the *p*-amino-*m*-sulfobenzoic acid salt of *p*-aminobenzoic acid. [e] Isolated partly as such and partly as the *p*-amino-*m*-sulfobenzoic acid salt of *p*-aminobenzoic acid. [f] The reduction was probably complete, in this case, in a much shorter time than is here indicated. Since there was no external evidence indicating just when the reduction phase was ended (as there was in all other cases) the heating was continued until we were sure that no unreacted nitro compound remained.

could be obtained. However, the relative amounts of these products varied widely, indicating that their formation is very probably largely governed by constitution factors. This is probably the most striking result of the present work. Without presuming to be arbitrary, since the evidence available at present is still not very extensive, we may recognize several definite influences. Thus it is apparent that a ring methyl group favors the formation of amines, while the presence of a carboxyl group, a second nitro group, or a condensed ring favors the formation of amino-sulfonic acids. In the few cases studied, the position of the second substituent seems to be of comparatively small influence.

In most cases, the combined yields of the two chief products (amine and mono-sulfonated amine) was slightly in excess of 80%. Only in two cases was it less. In the case of α-nitronaphthalene, the chief product was found to be an amino-disulfonic acid (isolated in 66% yield), and the total yield of this plus those of the two normal products was close to 95%. In the second case, that of nitrobenzene, we have not as yet succeeded in isolating a disulfonic acid. It is possible that the production of a very soluble disulfonic acid (extremely difficult to separate from the admixed inorganic salts) may account for the low total yield. We also believe it highly probably that in most of the other cases (that of *p*-nitrophenol is an exception, due to the inadequacy, in this case, of the methods used to isolate the product) the difference between the combined yields of the two chief products and 100% may be largely due to the occurrence of other very soluble amino-disulfonic acids, which we have not as yet attempted to isolate.

Another significant observation should be mentioned. It was noted that the speed of the first phase of the reaction (reduction) increased with dilution. This effect was particularly noted in experiments with nitrobenzene and with 2-nitro-1,4-xylene.[8] This led us to suspect that one of the early stages of the reaction is an *ionic* reduction, a suspicion which was lent further support by other observations. Thus it was noticed, in the case of α-nitronaphthalene, that the use of alcoholic aqueous media appreciably slowed down the reaction, contrary to expectation. It was also noted that neutral sodium sulfite was able to reduce dinitrobenzene in two hours, whereas bisulfite required over eight and one-half hours. All these observations can be reconciled with the view that for these reductions, the activity of the sulfite ion is of great importance.

On the contrary, however, it has been determined that partially neutralized sodium bisulfite is more effective in these reactions than normal

[8] It should be mentioned that the velocity of the first phase of the reaction (usually a heterogeneous reaction) depended upon the efficiency of agitation. However, it was attempted to keep this factor as constant as possible, and the results recorded are therefore comparable.

sodium sulfite. At present we can harmonize this with the above observation relative to dinitrobenzene only by the assumption that another stage in the reduction is favored by higher hydrogen-ion concentration than is furnished by neutral sulfite, and that this factor, in the case of dinitrobenzene, is of secondary importance, for some reason which is not as yet clear. In this connection it should also be stated that the addition of alkali had little or no effect upon the speed of reduction of α-nitronaphthalene. Completely neutralized bisulfite and un-neutralized bisulfite, in this case, were about equally effective. We hope to throw more light upon these problems by virtue of further investigations now being carried out in this Laboratory.

Experimental Part

Experiments with α-Nitronaphthalene

(A) **With Bisulfite and Aqueous Alcohol.**—Twenty-five grams of α-nitronaphthalene (m. p. 57–57.5°), 76 cc. of 5.2 *N* sodium bisulfite (15% excess), 100 cc. of 95% alcohol, and 200 cc. of water were heated under a reflux condenser. At the boiling point of the solution the reduction was incomplete at the end of thirteen hours. By working up the mixture there was obtained 9.5 g. of naphthionic acid, 7 g. of α-nitronaphthalene (unchanged), and 0.8 g. of α-naphthylamine; yields (on the basis of the nitro compound used): amine, 10%; aminosulfonic acid, 58%.

(B) **With Aqueous Bisulfite.**—A typical run is given. Thirty-five grams (0.2 mole) of α-nitronaphthalene, 200 cc. of 5.2 *N* sodium bisulfite (75% excess) and 250 cc. of water were heated under a return condenser until the mixture was completely homogeneous. The contents of the flask, evaporated to 300 cc. and treated with 50 cc. of 12 *N* hydrochloric acid, gave a heavy white precipitate, which was filtered from the cooled solution. This mixture was warmed with 300 cc. of water, which dissolved the salts present, leaving the naphthionic acid (soly., 0.024 g. in 100 cc. of water); 13.5 g. (29%) of the aminosulfonic acid was thus obtained.

The combined filtrates were saturated with sodium chloride, and the precipitate produced was filtered off. It was nearly free from inorganic salts. When dry it weighed 31 g., which, on the basis of a monosodium salt of a naphthylamine disulfonic acid is equivalent to a yield of 66%.

(C) **With Aqueous Bisulfite and Alkali.**—Thirty-five grams was reduced according to the standard procedure. The reduction required five hours. Acidification with 50 cc. of 12 *N* hydrochloric acid gave 10 g. (22%) of naphthionic acid. Seventy-five grams of stick sodium hydroxide was added to the combined filtrates and steam passed through, giving 0.5 g. or 2% of α-naphthylamine (m. p. 48–48.5°). The residue was made acid and was again distilled with steam, but no volatile substance was present, and therefore no naphthol was produced during the reaction.

Identification of the Products.—α-Naphthylamine was identified by melting point and mixed melting point with a sample of known purity. Naphthionic acid was identified by conversion to the diazonium salt, according to the method of Erdmann.[9] The diazonium salt thus obtained decomposed instantaneously at 140.5°. It gave characteristic azo dyes with alkaline β-naphthol and with phenol.

A sample of the monosodium salt of the naphthylamine disulfonic acid was crystallized four times from 70% alcohol. It still retained a slight pinkish tint, but was completely free from inorganic salts. It was dried at 140° and analyzed.

[9] Erdmann, *Ann.*, **24**, 330 (1888).

Anal. Calcd. for $C_{10}H_8S_2O_6Na$: S, 19.68; Na, 7.07. Found: S, 19.28; Na, 6.94, 7.00.

It is almost certain from these analyses and the method of synthesis that this compound is the monosodium salt of 1-aminonaphthalene-2,4-disulfonic acid, described in an early German patent.[10] No further time was spent on its orientation at this time, as we were interested only in the groups introduced by the reagent and not in their positions.

Experiments with Nitrobenzene

(A) The Standard Procedure.—Fifty grams was reduced in one and one-half hours. The contents of the flask were evaporated to 500 cc., decomposed with 100 cc. of concentrated hydrochloric acid, and re-evaporated to 500 cc. One hundred and twenty grams of solid sodium hydroxide was then immediately added, and the mixture steam distilled. The distillate, on extraction with ether, drying of the ethereal extracts, and distillation, gave 7 g. of aniline, boiling at 181–183° (16%, on the basis of the nitro compound used). The residue from the distillation was filtered, while still hot, from precipitated inorganic salts (sodium chloride and sodium sulfate). On cooling the filtrate to room temperature, crystals were obtained which were rendered almost colorless by repeated washing on the filter with methyl alcohol. These were nearly pure sodium sulfanilate, and when dry, weighed 38 g. (35%).

(B) Bisulfite Followed by Sulfuric Acid.—The standard procedure was followed, using 50 g. of the nitro compound. The reduction stage again required one and one-half hours.[11] One hundred cc. of concentrated sulfuric acid was used to decompose the solution. There were obtained 16 g. (20%) of sulfanilic acid and 12 g. (32%) of pure aniline.

Identification of Sodium Sulfanilate.—Bromination with liquid bromine gave tribromoaniline, identified by melting point and mixed melting point with a reliable specimen. The phosphorus pentachloride reaction product[12] was prepared by heating the sodium salt with phosphorus pentachloride in dry benzene. It melted at 154–155°, whereas the "trichloro compound" of Laar, when very pure, melts at 158°. Oxidation of the sodium salt with chromic acid and sulfuric acid in a current of steam gave benzoquinone, m. p., 113°; mixed m. p. with known sample of quinone, 113°. A purified sample of the sodium salt was analyzed, after drying at 140°.

Anal. Calcd. for $C_6H_6NSO_3Na$: Na, 11.53. Found: Na, 11.77.

Experiments with *p*-Nitrotoluene

Fifty grams was reduced, according to the standard procedure, in five hours. The mixture was evaporated to 500 cc., and decomposed with 100 cc. of 12 *N* hydrochloric acid. After re-evaporating to 500 cc., the solution was cooled, 100 g. of sodium hydroxide dissolved in 100 cc. of water was added, and this mixture was distilled with steam. From the distillate, 30.5 g. (72%) of nearly pure *p*-toluidine was obtained (m. p., 44.5°; b. p., 198–199°; acetyl derivative, m. p., 147–147.5°). The residue from the steam distillation deposited, on cooling, a white organic salt mixed with sodium chloride and sodium sulfate. This was dissolved in water, filtered hot, and the cooled filtrate acidified with hydrochloric acid. Eight grams (11%) of 4-toluidine-3-sulfonic acid was obtained.

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[10] Meister, Lucius and Brüning, German Patent 92,082, *Friedländer*, **4**, 528 (1895).

[11] In one run the standard procedure was varied by diluting with 2000 cc. rather than the usual 500 cc. of water. At this dilution the reduction stage required only forty minutes. A 25% yield of sulfanilic acid was obtained.

[12] Laar, *J. prakt. Chem.*, [2] **20**, 250 (1879).

Identification of the Aminosulfonic Acid.—Bromination gave 3,5-dibromo-4-toluidine, m. p., 70–71°. A sample prepared by bromination of *p*-toluidine melted at 74–75°. A mixture of the two melted at 72–73°. The sodium salt (from the aminosulfonic acid and excess dilute sodium hydroxide) lost no weight when heated at 150°. It was analyzed for sodium.

Anal. Calcd. for $C_7H_8SO_3NNa$: Na, 10.99. Found: Na, 10.80, 10.92.

Experiments with *o*-Nitrotoluene

Using the standard procedure, the reduction required twelve hours. After treatment with 100 cc. of 12 *N* hydrochloric acid, the mixture was allowed to cool. Large, white, silky plates separated, which were filtered. When dry, they weighed 11 g., and proved to be sodium *o*-toluene-sulfaminate. That this salt should precipitate from a solution which was both hot and quite strongly acid was rather unexpected. The filtrate was now boiled on the steam-bath for an hour, cooled again, treated with 100 g. of solid sodium hydroxide, and steam distilled. By extracting the distillate with ether, and evaporating the ether, there was obtained 17 g. (40%) of *o*-toluidine, boiling at 196–197°; acetyl derivative, m. p., 106–106.4°. The distillation residue was filtered, while hot, from inorganic salts. On cooling, white, lustrous, scaly crystals of sodium 2-toluidine-5-sulfonate were deposited. After drying at 90°, they weighed 27.5 g., or 34% of the calculated yield.

Identification of the Sodium Sulfaminate.—This salt, when heated at 140–150°, decomposed, losing 23–24% of its weight, and giving a strong toluidine odor. A sample, purified until free from sulfate, was boiled with hydrochloric acid, after which it gave a heavy precipitate of barium sulfate when treated with barium chloride, and when made alkaline, it gave a positive carbylamine test, indicating the presence of a primary amine. A diazotized sample gave dyes of the same shade as a known solution of diazotized sodium *o*-tolyl-sulfaminate.

Anal. Calcd. for $C_7H_8NSO_3Na \cdot H_2O$: Na, 10.13. Found: Na, 10.04, 10.15.

Identification of the Sodium Salt of the Amine Sulfonic Acid.—*Anal.* Calcd. for $C_7H_8NSO_3Na$: Na, 11.01. Found: Na, 11.10, 11.13. Oxidation with chromic acid in sulfuric acid gave toluquinone, m. p. 67.5°; m. p. of known sample of toluquinone, 66.5°; mixed m. p., 66.5°. Acidification of a concentrated water solution yielded the free sulfonic acid, which gave reactions characteristic of a substance of its type. Toluquinone was obtained from it, by oxidation as above.

Experiments with 2-Nitro-1,4-xylene

Preparation of 2-Nitro-1,4-xylene.—*p*-Xylene was nitrated according to Willstätter's chloroform method.[13] Ten grams of the hydrocarbon was nitrated at one time. Fractional distillation of the oil resulting from ten nitrations gave 73 g. of 2-nitro-1,4-xylene, boiling at 238–242° (740 mm.).

Reduction of 2-Nitro-1,4-xylene.—Thirty and seven-tenths g. (0.2 mole) was reduced, using the standard procedure except that 1000 cc. of water was added instead of the usual 300 cc. The products were as follows: 14.8 g. (60%) of 1,4-xylidine (b. p. 218.5°, corr.; acetyl derivative, m. p. 139.7–140°); and 6.2 g. (15.5%) of 2-amino-1,4-xylene-5-sulfonic acid.

Identification of the Aminosulfonic Acid.—The diazotized acid gave the usual coupling reactions. 1,4-Xyloquinone was obtained by oxidation with chromium trioxide and dilute sulfuric acid, and identified by the method of mixed melting points. The sodium salt was obtained from the free acid and excess sodium hydroxide as white

[13] Willstätter, *Ber.*, **42**, 4151 (1909).

scale-like crystals, containing two molecules of water of crystallization. Heated at 50–60° it loses one molecule of crystal water, and at 140–150° it loses the second molecule of water. Although Nolting, Witt and Forel[14] and also Nolting and Kohn[15] reported that the salt crystallized water-free, our results indicate that this is not the case.

Anal. (air-dried salt). Calcd. for $C_8H_{10}NSO_3Na \cdot 2H_2O$: Na, 8.87. Found: Na, 8.80, 8.66, 8.77, 8.91, 8.75. (50° dried salt.) Calcd. for $C_8H_{10}NSO_3Na \cdot H_2O$: H_2O, 7.47. Found (by heating at 150° to constant weight): H_2O, 7.51, 7.46. (150° dried salt.) Calcd. for $C_8H_{10}NSO_3Na$: Na, 10.33. Found: Na, 10.46, 10.48.

Experiments with *m*-Dinitrobenzene

(A) **Reduction with Neutral Sulfite.**—The procedure approximated to that used previously by Nietzki.[16] Forty-three grams of *m*-dinitrobenzene and 400 cc. of a solution (5.2 *N*) of sodium bisulfite (10% excess on the basis of the reduction of one nitro group) was heated just above the melting point of the solid until, upon cooling, no dinitrobenzene precipitated (two hours). One hundred and twenty-five cc. of 12 *N* hydrochloric acid was then added and the mixture boiled for thirty minutes. Yellow needles of *m*-nitraniline sulfonic acid separated, which weighed, when dry, 35 g. or 64% of the calculated quantity. They were purified by repeated reprecipitation, with hydrochloric acid, from a sodium hydroxide solution; followed by two recrystallizations from water, and thorough washing on the filter with methyl alcohol. They were dried at 140° and analyzed.

Anal. Calcd. for $C_6H_6O_6N_2S$: S, 14.62. Found: S, 14.16, 14.14.

The filtrate from which the *m*-nitraniline sulfonic acid separated was made alkaline with sodium hydroxide, the Glauber's salt was filtered off, and the filtrate was extracted with ether. Evaporation of the ether left a small amount of long needles, m. p. 110–112°; m. p. of *m*-nitraniline, 114°.

(B) **Reduction with Bisulfite.**—Seventy-two grams of the dinitro compound was heated for eight and one-half hours with 500 cc. of 5.2 *N* sodium bisulfite (110% excess for the reduction of one nitro group), and 500 cc. of water. One hundred cc. of concentrated sulfuric acid was then added. The cooled solution, after evaporation to 500 cc., contained a black cake of solid. This was extracted, first with hot 95% alcohol, and then with hot water. The part insoluble in water was discarded. From the alcohol solution was obtained 5 g. of unchanged dinitrobenzene. From the water solution was obtained about a gram of a substance, which, from its properties and a sulfur analysis on the crude material, was found to be the *m*-nitraniline-*p*-sulfonic acid. The filtrate from which this precipitated, on standing in a total volume of 400 cc. for several days, deposited purplish colored crystals, weighing 20 g. They were purified from admixed sodium sulfate by extraction with cold water, leaving 8 g. of an organic substance, which proved to be 1,3-diaminobenzene-4-sulfonic acid. It was identified by its amphoteric nature, the readiness with which it could be diazotized, and its crystalline habits. It crystallized in two distinct modifications—large monoclinic plates and elongated prisms.[17]

Anal. Calcd. for $C_6H_8N_2SO_3$: S, 17.00. Found: S, 16.66, 16.40.

Experiments with *p*-Nitrophenol

The standard procedure was used, except that solid sodium hydroxide was added, equivalent to the phenol used, and in addition to the alkali added normally. From 55.6

[14] Nolting, Witt and Forel, *Ber.*, **18**, 2667 (1885).

[15] Nolting and Kohn, *ibid.*, **19**, 141 (1886).

[16] Nietzki, *Ber.*, **29**, 2448 (1896).

[17] *Cf.* Post, *Ann.*, **205**, 105 (1880).

g. of *p*-nitrophenol, 10.5 g., or 14% of the theoretical weight of *p*-aminophenol-*m*-sulfonic acid, was obtained, by extracting the mixture of salts obtained after the acid treatment with water at 30°, and filtering the insoluble portion. It was impossible to isolate any other product, or to increase the yield of the aminosulfonic acid. It is probable, however, that the aminosulfonic acid is the chief product of the reaction, but it is impossible to isolate more of it without resorting to a laborious series of fractional crystallizations of the mixture obtained after the usual acid treatment. (The aminosulfonic acid is soluble in water to the extent of about 3 parts per 100.) Evidence was obtained which indicated the presence of considerable quantities of the aminophenol sulfonic acid in later crystalline fractions and mother liquors. Thus, the pure aminophenolsulfonic acid shows an interesting and characteristic fluorescence—violet in pure water, and bluish-purple in alkaline solution. The acidified solutions do not fluoresce. Now, in an attempt to separate more of the product from the inorganic salts produced in the reaction, after acid treatment, by a process of fractional crystallization, it was noted that all succeeding crystalline fractions, mother liquors, and filtrates showed this same fluorescence. Furthermore, other typical color reactions of this compound persisted throughout these later fractions. Moreover, solutions of *p*-aminophenol (the other expected product) in aqua ammonia are lavender and do not fluoresce. This affords evidence that very little, if any, of this amine is produced, and that the amount of aminosulfonic acid isolated constitutes but a minimum yield.

Identification of the Aminophenol Sulfonic Acid.—This substance, when heated with 25% sulfuric acid in a sealed tube for six hours at 165–170°, gave *p*-aminophenol, m. p., 183–183.5° (decomp.); m. p. of a sample of *p*-aminophenol of known origin, 183.4–183.8° (decomp.); mixed m. p. 182.8–183.2° (dec.). The aminophenol sulfonic acid gave a diazonium sulfate which did not decompose upon boiling with water. This is in accord with the observation of Schultz and Stable,[18] who state that the diazo compound of this aminophenol sulfonic acid is stable toward boiling water. Our diazo salt melted at 171°, after two crystallizations from water. Schultz and Stable report a melting point of 189°. The diazo compound, when heated with 25% sulfuric acid in a sealed tube at 180° for two hours, gave hydroquinone, identified by the method of mixed melting points.

Experiments with *p*-Nitrobenzoic Acid

Twenty-five grams was reduced according to the standard procedure, except that sodium hydroxide was again added in quantity sufficient to convert the acid to its sodium salt. The reduction stage required four and one-half hours. Fifty cc. of 12 *N* hydrochloric acid was then added and the mixture boiled again for two and one-half hours. Upon cooling, a fluffy, white solid separated, weighing 11 g., when dry. This was shown to be the *p*-aminobenzoic acid salt of *p*-amino-*m*-sulfobenzoic acid. The filtrate was evaporated to 250 cc. and allowed to stand. A second solid substance separated, weighing, when dry, 6 g.[19] This was shown to be *p*-aminobenzoic acid sulfate. On further evaporation of the filtrate to 150 cc. and cooling to −10°, a precipitate of 37 g. of Glauber's salt was obtained, and 40 g. more was thrown out by the addition of 250 cc. of 95% alcohol. The Glauber's salt was extracted with hot methyl alcohol. Evaporation of the alcohol left 1.5 g. of *p*-aminobenzoic acid sulfate. Three grams more was obtained by evaporating the aqueous ethyl alcoholic filtrate to 50 cc., extracting the resulting

[18] Schultz and Stable, *J. prakt. Chem.*, [2] **69**, 336 (1904).

[19] In another run, the filtrate was divided into two parts at this point. One part was extracted with ether as it was, but gave no appreciable ether-soluble material. The other part was made feebly alkaline, and then extracted with ether. Three grams of *p*-aminobenzoic acid was obtained.

precipitate of impure sodium chloride with hot methyl alcohol, and expelling the alcohol. The filtrate was now evaporated to dryness, the residue extracted with hot 95% ethyl alcohol, the alcohol evaporated to a volume of 25 cc. and cooled. A precipitate of 0.5 g. of *p*-aminobenzoic acid, melting, without purification, at 183–185°, was obtained.

Properties of the *p*-Aminobenzoic Acid Salt of *p*-Amino-*m*-sulfobenzoic Acid.—This is an acidic salt, which burns completely without melting. It is soluble in dilute alkali, and is reprecipitated unchanged by dilute acids. It is insoluble in acids, dilute or concentrated, and in ordinary organic solvents. It is practically insoluble in cold water, but appreciably soluble in hot water. Qualitative tests showed that it is neither an amine sulfate nor an amine hydrochloride. It crystallized from water in needles, showing a silky, fibrous nature under the microscope. A sample was purified for analysis by repeated reprecipitation from an alkaline solution (both ammonium and potassium hydroxides were used) with dilute hydrochloric acid, and then by repeated crystallization from water. It was then washed repeatedly on the filter with methyl alcohol and dried at 140°. The analytical results agree most closely with those calculated for a salt consisting of one molecule of *p*-aminobenzoic acid and one molecule of *p*-amino-*m*-sulfobenzoic acid.

Anal. Subs., 0.2747, 0.2982, 0.3005, 0.2627, 0.3865: $BaSO_4$, 0.1704, 0.1831, 0.1826, 0.1607, 0.2407. Subs., 0.1391, 0.1159: CO_2, 0.2378, 0.1988; H_2O, 0.0543, 0.0422. Calcd. for $C_{14}H_{14}O_7N_2S$: C, 47.5; H, 4.2; S, 9.04. Found: C, 46.7, 46.9; H, 4.0, 4.3; S, 8.53, 8.45, 8.35, 8.37, 8.55. *Titration equivalent.* Subs., 0.4376, 0.4355: 0.2230 *N* NaOH (phenolphthalein), 16.79, 16.60 cc. Calcd. for $C_{14}H_{14}O_7N_2S$ (tribasic): 16.61, 16.53 cc.

This insoluble salt was split into its components as follows. To 1.1664 g. of an analytically pure sample was added 29.54 cc. of 0.2230 *N* sodium hydroxide, the exact amount calculated to neutralize two mono-acidic groups of a molecule of molecular weight 354. A slight insoluble portion was brought into solution by adding a little water. The solution showed an acid reaction toward litmus. It was extracted thirteen times with ether. The thirteenth extract, evaporated separately, gave 0.003 g. of the ether-soluble material. In all 0.401 g. of this material (*p*-aminobenzoic acid, m. p. 184–185°) was obtained.

Titration equivalent. 0.2301 g. required 7.63 cc. of 0.2230 *N* NaOH. Calcd. for $C_7H_7O_2N$ (monobasic), 7.54 cc.

To the water solution was added hydrochloric acid until a precipitate formed. This weighed 0.1152 g., after drying at 80° and required 4.36 cc. of 0.2230 *N* NaOH. Calcd. for $C_{14}H_{14}O_7N_2S$: 4.37 cc. Thus it appears that thirteen extractions with ether did not remove quite all of the *p*-aminobenzoic acid. When acid was added, this precipitated as the *least soluble salt* of the ions present in the solution, namely, as the amino-sulfobenzoic acid salt. Since 0.115 g. of this salt is equivalent to 0.044 g. of *p*-aminobenzoic acid, the total yield of the latter was 0.401 + 0.044 = 0.445 g.; calculated for 1.1664 g. of the salt, 0.451 g.[20] The filtrate, after separation of the salt, was evaporated to a small volume. This gave 0.51 g. of a white substance (dried at 115°). This was a sulfur-containing acid which crystallized from water in small plates characteristic of *p*-amino-*m*-sulfobenzoic acid.[21]

Titration equivalent. 0.2659 g. required 10.90 cc. of 0.2230 *N* NaOH. Calcd. for $C_7H_7O_6NS$ (dibasic): 11.00 cc.

[20] In a previous run, in which only three extractions with ether were made, 0.27 g. of aminobenzoic acid as such, and 0.155 g. as the reprecipitated salt, or a total of 0.425 g., was obtained from 1.116 g. of the substance; calculated, 0.432 g.

[21] *Cf.* Van Dorssen, *Rec. trav. chim.*, **29**, 373 (1910); Scott and Cohen, *J. Chem. Soc.*, **123**, 3180 (1923).

Identification of *p*-Aminobenzoic Acid Sulfate.—A sample was dissolved in the least possible *N* potassium hydroxide, and carefully acidified with 2 *N* hydrochloric acid. At the neutral point, a substance precipitated which was identified as *p*-aminobenzoic acid by mixed melting points. With bromine water it gave tribromoaniline and an ammonia soluble substance. The latter, after reprecipitation with acid, showed a decomposition range of 266–286°. (Reported by Sudborough for dibromo-*p*-aminobenzoic acid, 260–270°.)

Summary

1. A number of aromatic nitro compounds have been reduced with sodium bisulfite, and the solutions thus obtained have been boiled with mineral acids.

2. The quantities of amines and aminosulfonic acids which are produced in this manner have been determined.

3. Several other reduction products have been isolated and identified.

4. A standard procedure for studying the Piria reaction has been adopted, and comparable results thereby obtained.

5. Factors have been pointed out which affect the reaction and require further investigation.

MINNEAPOLIS, MINNESOTA

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[Contribution from the School of Chemistry of the University of Minnesota]

THE PIRIA REACTION. II. THE ROLE OF THE SULFAMINIC ACIDS[1,2]

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When the acid treatment which follows the reduction of a nitro compound in the "over-all" Piria reaction[3] is omitted, the principal product which can be isolated is a sulfaminic acid salt, of the general formula $RNHSO_3M$. The isolation of an N-sulfonated compound of this type was included among the original findings of Piria,[4] and thereafter similar products were mentioned by other early investigators.[5] However, that these sulfaminic salts were the *chief* products of the reaction when acid treatment was avoided was first emphasized by Weil,[6] who investigated a variety of aromatic nitro compounds, including alkyl nitrobenzenes,

[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Murray M. Sprung in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September 1928.

[2] Presented before the Division of Organic Chemistry of the American Chemical Society at the Minneapolis Meeting, September 9–16, 1929.

[3] Hunter and Sprung, This Journal, **53**, 1432 (1931).

[4] Piria, *Ann.*, **78**, 31 (1851).

[5] Hilkenkamp, *ibid.*, **95**, 86 (1885); Smit, *Ber.*, **8**, 1442 (1875).

[6] (a) Weil, German Patents 147,552 and 151,134, *Friedländer*, **7**, 58, (b) 61 (1902); (c) Weil and Moser, *Ber.*, **55**, 732 (1922); (d) Weil and Wassermann, *ibid.*, **55**, 2533 (1922).

the alkyl esters of nitrocarboxylic acids, acylaminonitro compounds, nitrophenols, nitroamines and halogenated nitro compounds.

This consideration alone suggests a reasonable mechanism for the course of the "over-all" Piria reaction, which may be stated as follows: in the reduction stage, the nitro group is reduced to an amine or a sulfaminic acid or both; in the acid treatment stage, the sulfaminic acid is partly hydrolyzed to sulfuric acid and the same amine, and is partly rearranged to an aminosulfonic acid. In fact, it was this simple conception of the reaction which we set up as a working hypothesis at the start of our work. It is readily suggested by two considerations.

1. Many investigators have shown that the salts of sulfaminic acids are converted into aminosulfonic acids by baking, and in one or two cases the same is true of the free acid.[7]

2. Weil especially[6b] has pointed out that the addition of concentrated mineral acid aids the transformation of sulfaminic acids to the aminosulfonic acid derivatives. In more or less vague terms, other investigators have mentioned the same reaction.[8]

Against the hypothesis must be considered four opposed considerations.

1. The statement of certain investigators that "dilute" mineral acids hydrolyze the sulfaminic acids quantitatively,[9] though we were unable to find any who stated the concentration of acid used, or gave any quantitative data in support of this contention.

2. Weil himself, in another place,[6b] explicitly states that he does not believe that the sulfaminic acids are transformed into the aminosulfonic acids. He suggests that sulfonation may actually occur in the reduction stage, but offers no experimental evidence, nor any theoretical reason for his opinion.

3. Raschig[10] has suggested a mechanism of formation of sulfaminic acids and amino sulfonic acids, from a hypothetical common intermediate, an arylimino disulfonate, $ArN(SO_3Na)_2$.[11]

[7] Junghahn, *Ber.*, **35**, 3747 (1890); Seyewitz and Block, *Bull. soc. chem.*, [4] **1**, 320 (1907); Seyewitz and Noel, *ibid.*, [4] **3**, 497 (1908); Quilico, *Gazz. chim. ital.*, **56**, 620 (1926); De Ruijter de Wildt, *Rec. trav. chim.*, **23**, 173 (1904); Bamberger and Hindermann, *Ber.*, **30**, 654 (1897).

[8] We know of only one set of experiments concerning the effect of concentrated acids on sulfaminic acids which was both carefully performed and adequately reported, that of Bamberger and Kunze [*Ber.*, **30**, 2274 (1897)], who showed that potassium phenylsulfaminate, when treated with a few drops of concentrated sulfuric acid in glacial acetic acid and allowed to stand for eighty hours in the ice box, was converted to *o*-anilinesulfonic acid and that this, in turn, could be converted to sulfanilic acid by heating at 180–190° with concentrated sulfuric acid.

[9] See, for example, Traube, *Ber.*, **23**, 1653 (1890); *ibid.*, **24**, 360 (1891); Junghahn, *ibid.*, **31**, 1234 (1898).

[10] Raschig, "Stickstoff and Schwefel Studien," Verlag Chemie G. m. b. H., Berlin, **1924**, pp. 255–272.

[11] The isolation of a compound of this type has recently been reported by Engel

$$NaSO_3—Ar—NHSO_3Na \xleftarrow{\text{Rearr.}} ArN(SO_3Na)_2 \xrightarrow{\text{Hydrolysis}} ArNHSO_3Na$$

4. Disulfonic acids have been isolated at the end of the acid treatment stage,[12] and their presence is unaccounted for by any scheme ever suggested.

Viewing these conflicting ideas, it seemed that the first constructive step would be to ascertain, not whether sulfaminic acids could be rearranged, but whether they could be rearranged by acid of the concentrations ordinarily used in the acid treatment stage of the Piria reaction. Our own practice being to bring the reaction mixture to a concentration in the neighborhood of 2 *N* with respect to hydrochloric acid, it was decided to take representative sulfaminic acids and subject them to the action of a wide range of acid concentrations on each side of this point, in order to attain quantitative certainty on this single point. At the same time, it was planned that if two parallel reactions were actually found, kinetic studies would be carried out. The event showed, however, that over the range of concentration from about 0.5 to 5.35 *N*, only hydrolysis occurs. Though the opinion that the sulfaminic acids were not the precursors of the aminosulfonic acids has already been expressed, we believe that this is the first time that quantitative data of this type have been brought forward to settle the point.

Experimental Method

A definitely standardized procedure was employed. Several of the sodium salts of sulfaminic acids were prepared and purified. Weighed samples of these salts (contained in 50-cc. Erlenmeyer flasks) and measured volumes of a standardized hydrochloric acid were brought to temperature in a thermostat. Then the acid was added to the sulfaminate, the flask stoppered, and replaced in the thermostat until the reaction was complete.[13] The contents of the flask were then washed out into a beaker, heated to boiling and a boiling solution of barium chloride added. The precipitate of barium sulfate was filtered, washed, dried and weighed. The weight of sulfuric acid produced was calculated from the weight of the barium sulfate.

Materials

The sodium sulfaminates were prepared by the action of partially neutralized sodium bisulfite upon the corresponding nitro compounds, and [THIS JOURNAL, **51**, 3483 (1929)] in a paper dealing with the cleavage of azo compounds by alkali sulfites.

[12] For example, Walter, German Patent 109,487, *Friedländer*, **5**, 70 (1899); Bucherer and Borsch, *J. prakt. Chem.*, [2] **111**, 329 (1925); Meister, Lucius und Brüning, German Patent 92,082, *Friedländer*, **4**, 528 (1895); and numerous other patent citations.

[13] Preliminary runs, made to determine approximate speeds, indicated that with the most dilute acid used (*ca.* 0.5 *N*) the reactions were complete in about forty hours at 40°. The later runs were made in the neighborhood of 50°.

purified by repeated crystallization from water to which a few drops of alkali were added to prevent decomposition. In some cases it was impossible to free them entirely from admixed inorganic salts.

Sodium Phenyl Sulfaminate.—This is the most soluble of the salts used, and consequently was the most difficult to purify. After five recrystallizations from water, appreciable quantities of sodium chloride and sodium sulfate were still present. Therefore, to characterize the sulfaminate a small amount of the compound, further recrystallized until free from these salts, was dried for several days in a vacuum desiccator over calcium chloride. On analysis, it was found to contain one molecule of water of crystallization.

Anal. Calcd. for $C_6H_6NSO_3Na \cdot H_2O$: Na, 10.81. Found: Na, 10.85, 10.90.

The material which had been crystallized five times was then analyzed and found to contain 6.55% of sodium chloride, 4.78% of sodium sulfate and 13.99% of sodium, total. The composition of the sample was therefore as follows

Na_2SO_4, %.....	4.78, equiv. to 2.62% Na
NaCl, %.....	6.65, equiv. to 1.55% Na
$C_6H_6NSO_3Na \cdot H_2O$, %....	88.58, equiv. to 9.57% Na
Total	13.74% Na
Found by analysis,	13.99% Na

Sodium *p*-Tolyl Sulfaminate.—The salt was purified by several recrystallizations from water and dried in a vacuum desiccator for seven days.

Anal. Calcd. for $C_7H_8NSO_3Na$ (anhydrous): Na, 11.01. Found: Na, 11.19, 11.28.

There was still a slight admixture of sodium sulfate, which caused the sodium analysis to be higher than the theoretical. A 0.4-g. sample gave 0.0071 g. of barium sulfate, equivalent to 0.0030 g. of sulfuric acid, or 1.08% of sodium sulfate.

Sodium *o*-Tolyl Sulfaminate.—A sample was crystallized from water until free from sodium sulfate. It was dried in a vacuum desiccator over calcium chloride for four days.

Anal. Calcd. for $C_7H_8NSO_3Na$ (anhydrous): Na, 10.13. Found: Na, 10.25.

Sodium *p*-Acetaminophenyl Sulfaminate.—The salt was crystallized from water until free from inorganic impurities and dried *in vacuo* over calcium chloride for sixty hours. It contained two molecules of water of crystallization.

Anal. Calcd. for $C_8H_9O_4N_2S \cdot 2H_2O$: Na, 8.00. Found: Na, 8.18, 8.15.

Results

The sodium sulfaminates were allowed to react with solutions of hydrochloric acid varying in concentration from 0.47 to 5.35 *N*. The results thus obtained are presented in tabular form.

ANALYTICAL DATA ON THE REACTION BETWEEN SODIUM SULFAMINATES AND HCl[a]

Salt used	Runs	Sample, g.	Acid normality, max. and min.	H_2SO_4, calcd. for 100% hyd., g.
$C_6H_5NHSO_3Na \cdot H_2O$[b]	4	0.4	0.47–5.35	0.1755
p-$CH_3C_6H_4NHSO_3Na$[c]	3	.4	0.47–2.70	.1887
o-$CH_3C_6H_4NHSO_3Na$	3	.3	1.05–5.35	.1295
p $CH_3CONHC_6H_4NHSO_3Na \cdot 2H_2O$	4	.4	1.07–5.35	.1362

H_2SO_4 found, g. (av.)	Av. dev. from mean, g.
0.1765	0.0021
.1894	.0022
.1287	.0029
.1346	.0004

[a] The reactions were carried out at temperatures between 47–50°, varying not more than ±1° during a given run. [b] The sample contained 4.78% of sodium sulfate, as mentioned above. The sulfate due to this admixture was, of course, considered in the calculations. [c] The sample contained 1.08% sodium sulfate. The correction was applied as before.

For all four of these salts the quantity of sulfuric acid produced was therefore, within analytical error, the amount which should have resulted from complete hydrolysis of the sulfaminate to the corresponding amine and sulfuric acid. This was true for all acid concentrations.

According to the standard procedure used in the study of the "over-all" Piria reaction,[3] the solutions were approximately 2 normal with respect to hydrochloric acid, after the addition of this reagent. Since the quantitative experiments covered a sufficiently wide range of concentrations on either side of this figure, we consider this to be definite proof that sulfaminic acids play no part in the production of nuclear sulfonated compounds during the Piria reaction.

The investigations are being continued in the attempt to discover the intermediate which does give rise to the sulfonated amines.

Conclusions

Several sodium salts of sulfaminic acids have been prepared and carefully purified, and their reactions with varying concentrations of hydrochloric acid studied. It has been shown that with acid concentrations from 0.5 to 5.35 normal, these sulfaminates hydrolyze quantitatively to sulfuric acid and the corresponding amines, giving absolutely no trace of aminosulfonic acids.

Hence the aminosulfonic acids which are produced by the "over-all" Piria reaction are certainly not formed by rearrangement of sulfaminic acids.

It is worthy of passing notice that this work affords one more instance of a suspected indirect substitution, which in fact does not occur.

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